

X-ray fluorescence measurements of the organic antiferromagnet 2,4,6-triphenylverdazyl

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INTRODUCTION

Studying the class of stable free radicals called the verdazyls is of great interest because of their unusual magnetic properties. 2,4,6-triphenylverdazyl (TPV) shows weak ferromagnetism and antiferromagnetic ordering with a Neel temperature of 1.7 K [1] whereas 2,4,6-tri-p-tolylverdazyl (TTV) is paramagnetic [2]. According to Ref. [2] it can be due to different molecular packing, which leads to changes in the overlap of the orbitals that are occupied by unpaired 2p-electrons giving rise to different magnitudes of exchange interaction. A detailed study of the electronic structure of the organic antiferromagnet TPV is very important. In the present paper, we present results of soft X-ray fluorescence measurements of a TPV single crystal and compare our measurements with deMon density-functional theory (DFT) calculations. Evidence for a delocalization of unpaired N 2p-electrons over the verdazyl ring is found, which is in accordance with the spin density distribution of TPV. We show that intermolecular interactions are weaker than the intramolecular ones, which allows concluding that the electronic structure of TPV crystal has a quasi-one-dimensional character.

EXPERIMENTAL AND CALCULATION DETAILS

Single-crystal samples were grown by using recrystallization from an acetone solution. The crystals obtained have a hexagonal plate with its plane normal to the *a*-axis and its long edge along the *c* axis. Carbon and nitrogen K α (2p \rightarrow 1s transition) X-ray emission spectra (XES) were taken at beamline 8.0 of the Advanced Light Source, employing the University of Tennessee at Knoxville's soft X-ray fluorescence endstation. Photons with an energy of 298.7 eV, above the carbon K edge and with an energy of 400 eV, above the nitrogen K edge were delivered to the endstation via the beamline's spherical grating monochromator. The carbon and nitrogen K α spectra were obtained with an energy resolution of 0.5 and 1 eV, respectively.

The molecular structure of TPV consists of a verdazyl ring at the center surrounded by three phenyl groups with hydrogen side groups [2]. TPV molecules are arranged in zigzag chains along the *c* axes. TPV crystallizes in the orthorhombic structure with four molecules per unit cell, which

makes first principle band structure calculations extremely difficult. We have carried out deMon DFT program [3] calculations for one molecule by neglecting interchain interactions. The geometry of the radical compound 2,4,6,-triphenylverdazl (TPV) was optimized in the SCF calculation of unrestricted Hartree-Fock (UHF) equations by semiempirical MO AM1 method using MOPAC software [4]. The molecule includes a total amount of 41 atoms including 20 carbon atom, 4 nitrogen atoms and 17 hydrogen atoms (with a total of 165 electrons, total of 117 orbitals and (59 and 58) occupied α and β -orbitals, respectively).

In order to simulate the XES, we used the deMon DFT program. The intensity of carbon and nitrogen $K\alpha$ XES was obtained by summing populations (squares of the linear combination of atomic orbitals (LCAO) coefficients) of the atomic orbitals $\chi_{2p(A)}(r)$ centered on the given nitrogen or carbon atoms. We approximated the populations as obtained from the deMon DFT calculations of the TPV molecule with STO-3G basis set. Each peak in the theoretical XES spectra is also represented by a Gaussian lineshape function, with the same weight and full-width at half-maximum (FWHM = 1.3 eV) as the experimental spectra.

RESULTS AND DISCUSSION

The non-resonant carbon $K\alpha$ XES of TPV excited at $E_{\text{exc}}=298.7$ eV is shown in Fig. 1. The spectrum of benzene is also included for comparison. The fine structure of C $K\alpha$ XES of TPV resembles that of benzene because chemical structure of TPV consists of three phenyl groups. The calculated C $K\alpha$ spectrum reproduces the experimental one of TPV quite well. Good agreement between experimental C $K\alpha$ spectrum of the TPV crystal and calculated C $K\alpha$ spectrum of a model molecule shows that the intermolecular interactions are smaller than the intramolecular ones, which reveals quasi-one-dimensional electronic and magnetic properties of this compound. This conclusion is in agreement with electron spin resonance measurements of TPV [5], according to which line shape and line width are typical for a one-dimensional Heisenberg antiferromagnet.

The non-resonant N $K\alpha$ XES of TPV excited at around 400 eV is presented in Fig. 2 together with the calculated spectrum. We note that the spectral shapes of the experimental and calculated spectra are very similar. According to the calculation, unpaired N 2p-electrons are delocalized over the verdazyl ring, which was predicted in Ref. [2] based on the analysis of the magnetic properties

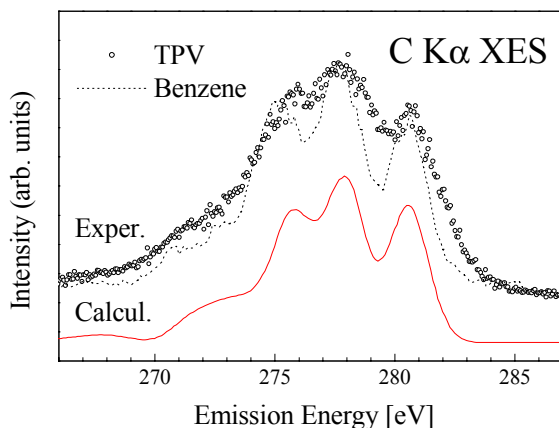


Fig.1 C $K\alpha$ XES of TPV and benzene and calculated C $K\alpha$ emission spectrum.

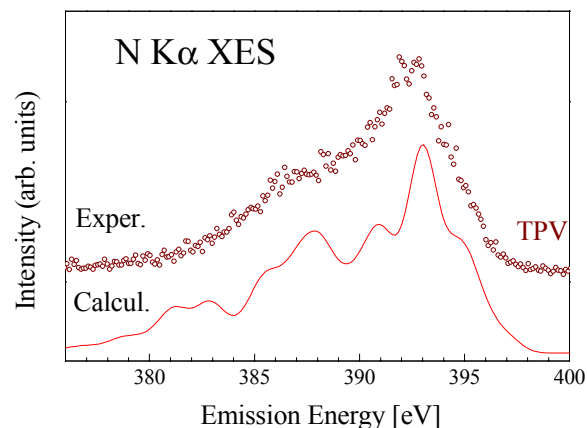


Fig. 2 N $K\alpha$ emission spectrum of TPV and calculated N $K\alpha$ emission for TPV.

of TPV. Azuma [2] pointed out that the spin density is distributed over four nitrogen atoms in the verdazyl ring, which implies the delocalization of the unpaired electron over the TPV molecule.

Therefore good agreement between experimental and calculated non-resonant N K α XES of TPV evidences the localization of unpaired electrons over the TPV molecule, which is considered as one of the most characteristic features of the magnetism of TPV [1].

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